

# Study of the Effect of Different Dopants on Optical Properties of ZnS Thin Films

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**Abstract:-** Pure ZnS thin films and doped with different dopants were prepared onto glass substrates by chemical bath deposition method. ZnS films were deposited using  $ZnCl_2$  as zinc ion source,  $SC(NH_2)_2$  as a sulfide ion source and Ammonia Hydroxide ( $NH_4OH$ ) to controlled PH value. the solution temperature is  $70C^\circ$  .

The transmission measurements were carried out in the wavelength range (300-2000) nm using (Jasco V-570 Double Beam) Spectrophotometer. The optical energy gap of prepared films were determined. It is 3.8eV for pure ZnS thin film. It was found that the energy band gap values of films doped with copper and antimony are greater than pure films, while its value for doping with silver is less than pure films.

Photoluminescence properties of of prepared films were studied. The photoluminescence spectra of the pure films are showed three peaks centered around (325,450 and 505) nm. The ZnS :Cu films had one peak at (323)nm. The ZnS:Ag films, also had three Peak centered around (329,440,460) nm. While the ZnS: Sb films, one peak is observed at (318) nm. It was found blue shift for peak centered around 325 nm when ZnS thin films were doped with copper and antimony, whereas a red shift in it for doping with silver.

**Keyword :** Zinc Sulphide, Pure , Doping .

## 1.INTRODUCTION

Zinc Sulphide (ZnS) is one of the II-VI semiconductor materials. ZnS thin films with wide bandgap (3.73 eV) which crystallizes in both cubic and hexagonal forms have recently received intensive attention to be used in many applications. It has relatively high refractive index and high transmittance in the visible range. ZnS compound is a promoting candidate for a large variety of applications including photonic crystal sensors, optical filters, light-emitting diodes, anti-reflection coatings, flat panel displays, phosphors and photovoltaic cells. ZnS is also an important phosphor host lattice material used in electroluminescent devices (ELD) [1,2].

Moreover , the content elements ZnS are nontoxic to the human body and are Very cheap and abundant [1,2,3] .

Previously, ZnS thin film have been deposited by many different techniques, thermal evaporation, self-assembly technique, spray pyrolysis, electron beam evaporation, Photochemical deposition (PCD), close-space sublimation , pulsed laser deposition, molecular beam epitaxy and chemical bath deposition [2]. Among the various methods, chemical bath deposition (CBD) is the most commonly used because of its simplicity, low cost, and coating large area of the semiconductor with good quality and high purity of deposited thin films. So, it was used in the present study to prepare ZnS thin films. The main goal of this present work is to study the influence of different dopants (Cu, Ag, Sb) on optical properties of ZnS thin films [2].

## 2. EXPERIMENTAL

ZnS thin films were deposited on glass substrates by chemical bath deposition technique. The cleaning of substrate plays an important role in deposition of thin film by CBD process. The substrates were cleaned with a soapy solution rinsed with distilled water and then with nitric acid followed by isopropanol, kept in an ultrasonic bath and finally rinsed with deionized water and dried in the air.

ZnS films were deposited chemically using 1M Zinc Chloride  $ZnCl_2$  as zinc ion source, 1M thiourea  $SC(NH_2)_2$  as a sulfide ion source and Ammonia Hydroxide ( $NH_4OH$ ) to controlled PH value. The total volume of the chemical bath was 100ml.

These solutions were mixed together in a separate beaker. Afterwards the mixed solution was stirred for 15 minutes. The pH value was maintained 11.6. When the deposition temperature reached  $70\pm 1^\circ C$ , pre-cleaned glass slides were introduced vertically inside the substrate holder, dipped into the solution and left for deposition for 180 minutes. After completion of film deposition, the samples were removed from the beaker and allowed to cool. The deposited films were then rinsed with de-ionized water to remove soluble impurities and dried in air. Schematic diagram for the deposition is shown in Fig. 1.

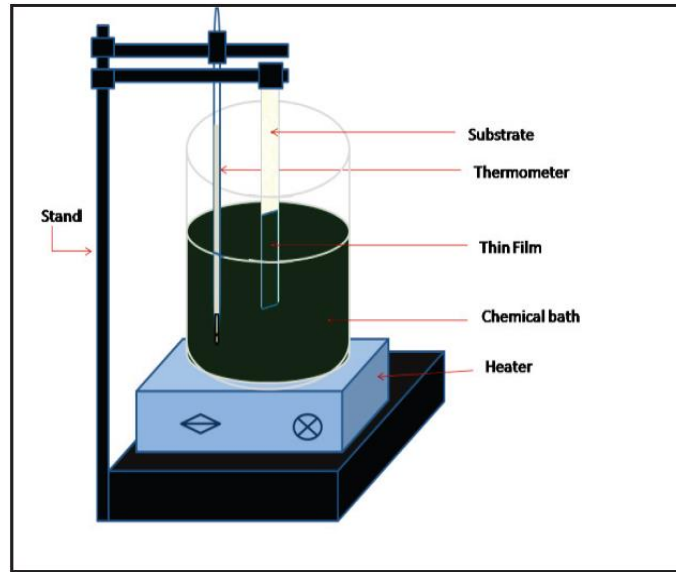
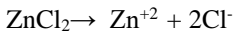
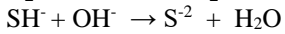
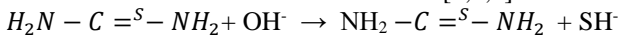
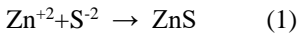


FIGURE 1.Schematic diagram of chemical bath deposition method.

The chemical reaction occurs as follows [4,5,6]:



Then the formation ZnS is according to equation:



The ZnS film thickness  $t$  is given by [7]:

$$t = \frac{\Delta m}{\rho A}$$

where  $\Delta m$  is the difference in mass before and after deposition,  $\rho$  is the bulk density, and  $A$  is the area of the film.

The optical measurements, which included transmission and absorption spectra in the wavelength range (300-2000) nm were carried out using (Jasco V-570 Double Beam) Spectrophotometer.

### 3. RESULTS AND DISCUSSION

#### Optical Properties

The transmission spectra of the prepared thin films in the wavelength range (300-2000) nm are illustrated in Fig. 2.

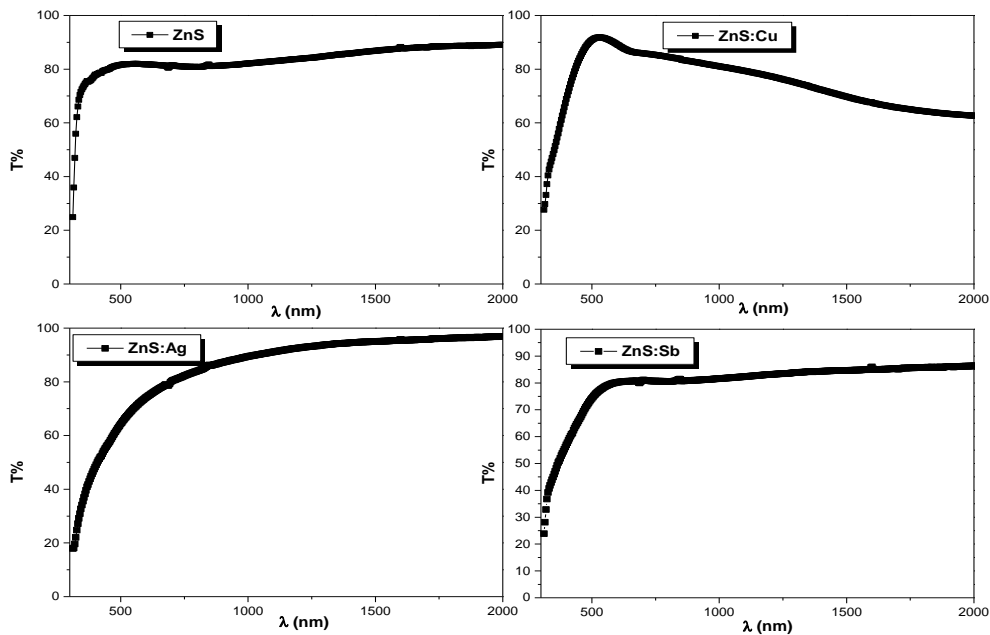


Figure 2. transmission spectra of the prepared thin films.

For more investigation, absorption coefficient  $\alpha(\text{cm}^{-1})$  of the ZnS thin films was determined from the transmittance measurements using Swanepoel's method [8,9]:

$$\alpha = 2.303 \frac{A}{t} \quad (2)$$

The nature of the transition (direct or indirect) was obtained by using the relation [10,11,12,13]:

$$ahv = A(hv - E_g)^n \quad (3)$$

where A is constant,  $\alpha$  is absorption coefficient and  $E_g$  is the band gap energy. For direct transition the n value is  $\frac{1}{2}$  whereas for indirect transition the n value is 2.

Band gaps were obtained by plotting  $(h\nu)$  against  $(\alpha h\nu)^2$  and extrapolating the linear part. By extrapolating the linear portions of the plots of  $(\alpha h\nu)^2$  versus  $h\nu$  to where  $(\alpha h\nu)^2 = 0$ , the value where the extrapolated line cuts energy  $(h\nu)$  axis is the band gap. The  $(\alpha h\nu)^2$  versus  $(h\nu)$  plot of pure and doped ZnS thin films with different dopants (Cu, Ag, Sb) are shown in Fig. 3, respectively.

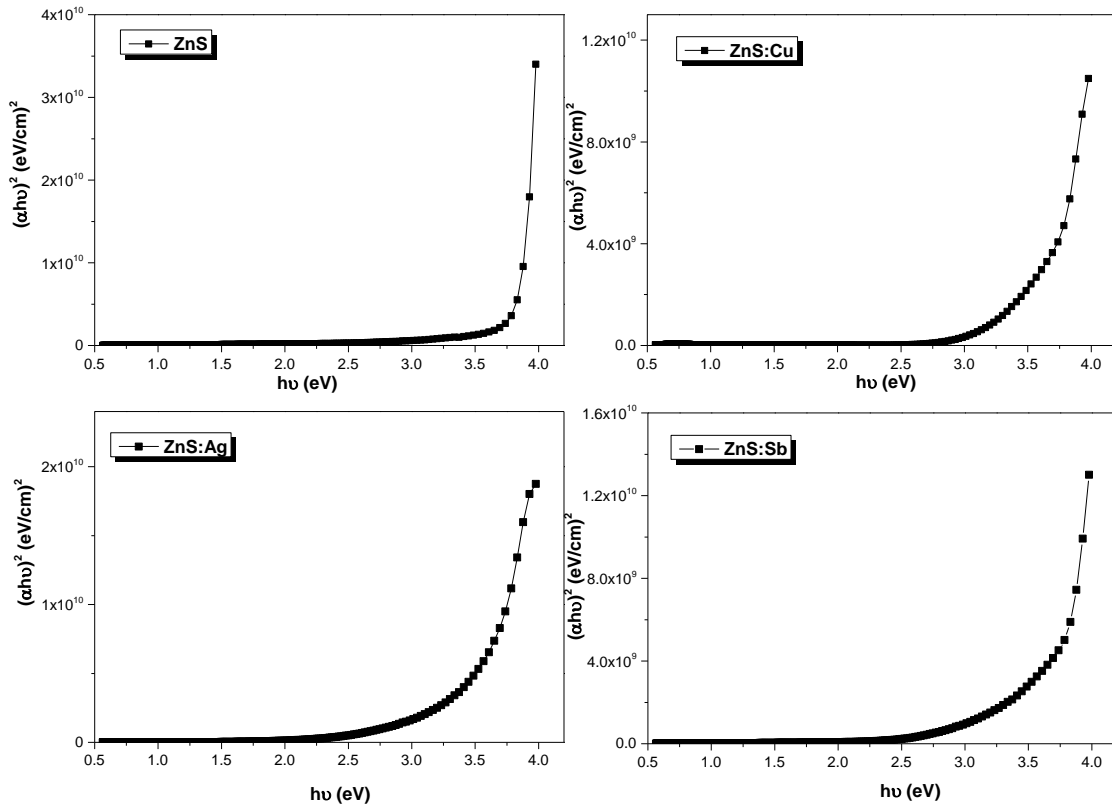


Figure 3. A plot of  $(\alpha h\nu)^2$  Vs.  $(h\nu)$  of pure and doped ZnS thin films.

The optical band gap value obtained from this plot is presented in Table 1. It is 3.8eV for pure ZnS thin film. This value of the optical energy gap is in good agreement with previously reported value.

The optical band gap ( $E_g$ ) value of doped ZnS thin films with (Cu, Ag, Sb) dopants are presented in Table 1.

impurity	pure	Cu	Ag	Sb
$E_g(\text{eV})$	3.8	3.85	3.78	3.9

It was found that the values of optical energy gap of the ZnS thin films doped with copper and antimony are greater than pure films, while its value for doping with silver is less than pure films. The increase in the band gap of Cu doped ZnS film can be related to the structural modification of ZnS thin film. It can also be supposed that the copper ions can replace either substitution or interstitial the zinc ions in the ZnS lattice creating the structural deformation.

On the other hand, the increase in the band gap or blue shift can be explained by the Burstein-Moss effect [14].

The Burstein-Moss effect results from the Pauli Exclusion Principle, and is seen in semiconductors as a shift with increasing doping of the band-gap defined as the separation in energy between the top of the valence band and the unoccupied energy states in the conduction band. The shift arises because the Fermi energy ( $E_F$ ) lies in the conduction band for heavy n-type doping (or in the valence band for p-type doping) [14]. While decreasing in the band gap of Ag doped ZnS can be attributed to the influence of near band levels. A small fraction of the Ag incorporated into ZnS lattice act as an acceptors and create localized levels near the valance band [20].

The increase in the band gap of ZnS after Sb doping can be explained by the Burstein-Moss effect.

### photoluminescence properties

The photoluminescence spectroscopy provides information about the structure, band gap, impurity levels, and localized defects in semiconductors thin film. So the room temperature photoluminescence spectra are recorded for pure and doped ZnS thin films in the spectral range of 300–650 nm. The PL spectra are shown in Fig. 3. The photoluminescence spectra (PL) of the pure ZnS films showed three peak centered around (325,450 and 505) nm. It is well known that the luminescent peak centered at 325nm could be assigned to the UV -excitonic emission . The ZnS thin Film reported previously have photoluminescence emission with bands in the range 450-505nm associated with Sulfur vacancy related donor and valence band [15,16,21]. One peak at (323) nm was observed for ZnS :Cu thin film related to the optical energy gap (3.85eV). It means that the Cu dopant made blue band shifts towards the short-wave part of spectrum [22]. Also, three Peak centered around (329,440,460) nm were observed for ZnS:Ag in Fig.3. the peak at 329nm corresponded to the energy band gap (3.78eV), while Photoluminescence emission With bands in the range (440 -460 nm) is associated with Sulfur vacancy [18,17,19] .

ZnS: Sb thin film showed one peak at (318) nm. It is assigned that the one peak is due to band gap of ZnS: Sb thin film. It is noticed that the optical energy gap maybe increase when it doped with copper and antimony but decrease with silver doping comparison with pure ZnS thin Film.

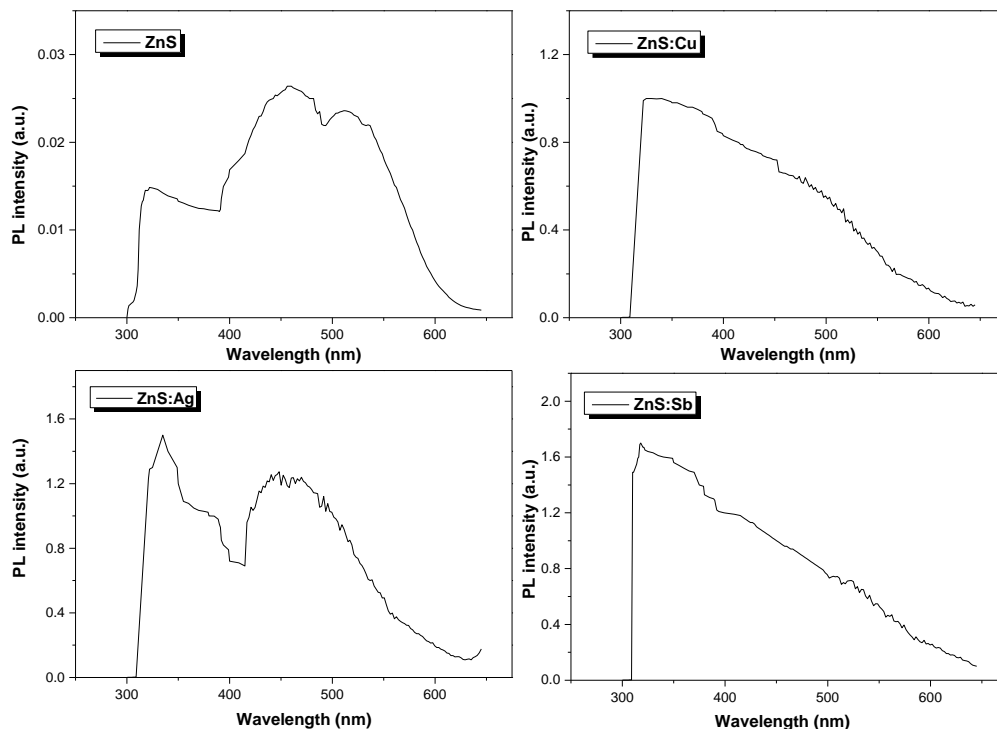


Figure 3. Photoluminescence Spectra of pure and doped ZnS thin films.

### CONCLUSION

Pure ZnS thin films and doped with different dopants were prepared on glass substrates by chemical bath deposition method. The optical Properties of these films were studied in range of 300-2000 nm. It was found that the optical energy of the ZnS thin films doped with copper and antimony are greater than pure films, while its value for doping with silver is less than pure films.

From Photoluminescence spectra of pure and doped ZnS thin films were Studied. It is Clear that The photoluminescence spectra (PL) of the pure ZnS films showed three peak centered around (325,450 and 505) nm. It was found blue shift for peak centered around 325 nm when ZnS thin films were doped with copper and antimony, whereas a red shift in it for doping with silver.

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